

Translated from Japanese by  
SCIENTIFIC TRANSLATION SERVICES  
411 Wyntre Lea Dr.  
Bryn Mawr, PA 19010

(19) Patent Office of Japan (JP)

(12) Patent Disclosure Bulletin (A)

(11) Patent Disclosure No.: 2001-19,681 (P2001-19681A)

(43) Disclosure Date: January 23, 2001 (01/23/2001)

(51) Int. Cl. <sup>7</sup> :	Identification Code	FI	Subject Code (Reference)
C07D 249/20	502	C07D 249/20 502	4L033
C09K 3/00	104	C09K 3/00 104 C	
D06M 13/35		D06M 13/55	
// D06M 101:00			
101:34			

Request for Examination: no requested  
pages 9)

No. of claims: 3

OL (Total

(21) Application No.: Hei 11-[1999]-195,358

(22) Application Date: July 9, 1999 (07/09/1999)

(71) Applicant: 591210839  
Osaka Seika Kogyo Co. Ltd.  
14-28, 7-chome, Sugihara, Higashi Yodogawa-ku, Osaka-shi, Osaka-fu

(72) Inventor: M. Tsutsumi  
13-27, 2-chome, Sugihara, Higashi Yodogawa-ku, Osaka-shi, Osaka-fu

(72) Inventor: H. Motomaru  
No. 104 Towa Raibutaun Sumiyoshi  
5-13, 3-chome, Kichito-cho, Higashi Nada-ku, Osaka-fu

(72) Inventor: K. Okawa  
4-9, Goban-cho, Hiyoshidai, Takagi-shi, Osaka-fu

(74) Agent: 100104581  
I. Miyazaki, Patent Attorney

F Term (Reference) 4L033 AB01 AC15 BA55

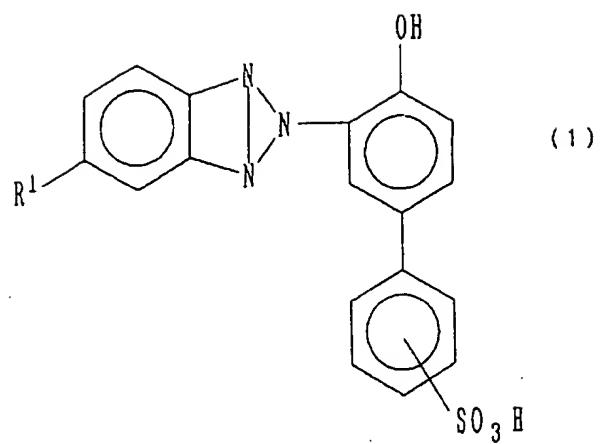
(54) [Title of the Invention] SULFONATED BENZOTRIAZOLE-TYPE COMPOUNDS

(57) [Abstract]

[Object] A light resistance promoting agent can be prepared easily and is highly resistant to the sunlight.

[Means for Accomplishing the Object] Sulfonated benzotriazole-type compound that can be represented by formula I given below and its salts.

[Chemical Formula 1]

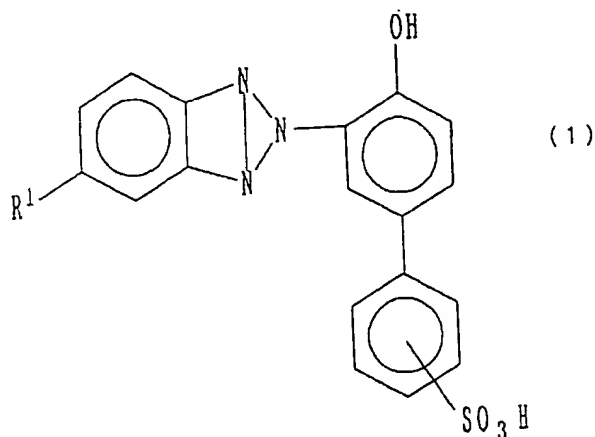


(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

## [Scope of the Patent Claims]

[Claim 1] Sulfonated benzotriazole-type compound that can be represented by formula I given below and its salts.

## [Chemical Formula 1]

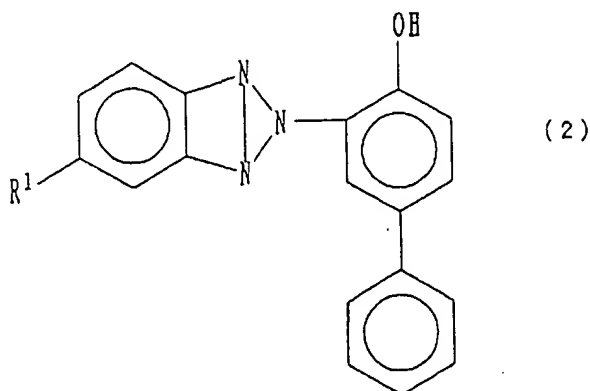


(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

[Claim 2] Sulfonated benzotriazole-type compound and its salts in accordance with claim 1 that can be used as a light resistance promoting agent for fibers and fiber products.

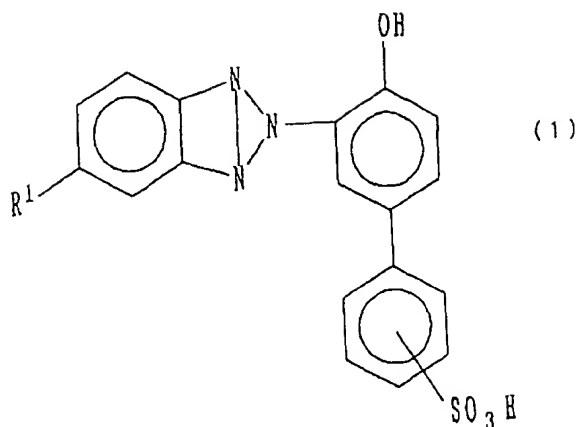
30 [Claim 3] Method for the synthesis of a sulfonated benzotriazole-type compound that can be represented by formula (1) given below and its salts, in which a benzotriazole-type compound that can be represented by formula (2) given below (in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom) is reacted with sulfuric acid and, if necessary, the compound thus obtained is converted to a salt form.

## [Chemical Formula 2]



(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

## [Chemical Formula 3]



20 (in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

## [Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention pertains to a new benzotriazole-type compound. More specifically, the present invention pertains to a benzotriazole-type compound that is useful as a light resistance promoting agent for fibers and fiber products.

[0002]

30 [Prior Art] A 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compound has been used as a stabilizer for preventing light-induced deterioration (light resistance promoting agent) of fibers and fiber products. Among the fibers mentioned above, polyamide-type fibers (nylon-type fibers) and such protein fibers as wools are usually dyed with an acidic dye (anion dye). The fiber products dyed with the acidic dye (e.g., textile goods) are used not only in clothing but also in interior products, sofas, chairs, curtains, etc. Such products are frequently exposed to the sunlight for a prolonged period of time. As the usable lifespan of a passenger car has extended in recent years, it has become desirable for seat and cover, etc. of passenger cars (especially high-class passenger cars) to be resistant to fading for a prolonged period of time (e.g., 5-7 years). Therefore, it has also become desirable that the light resistance promoting agent used for fibers and fiber products can maintain its effectiveness for a long period of time.

40 The benzotriazole-type compound used as the light resistance promoting agent for fibers and fiber products (color fading preventing agent) is in a sulfonated and water-soluble form and is used together with the dye in the same bath. Such a benzotriazole-type compound has to have high affinity and high dyeing property against fiber and fiber products. In addition, it should be resistant to the sunlight.

[0003] E.g., 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compounds with their 5' position sulfonated are described in Patent Disclosure No. Hei 1-[1989]-149,777. Such compounds are synthesized by sulfonation of a 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compound having a t-butyl group at its 5' position.

50 [0004] Moreover, 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compounds having an aryl alkyl group sulfonated at p position at their 3' or 5' position are described in Patent Disclosure No. Hei 3-[1991]-118,373. Such compounds are synthesized by sulfonation of a 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compound having an aryl alkyl group at its 3' or 5' position ( $\alpha,\alpha$ -dimethylbenzyl group, etc.).

[0005] In addition to the sulfonated benzotriazole-type compounds, such sulfonated benzophenone-type compounds as sulfonated 2-hydroxy-4-alkoxy benzophenone and such sulfonated triazine-type compounds as 2-(2'-hydroxyphenyl)-s-triazine having a sulfonic acid have been developed as a light resistance improving agent for fibers (polyamide-type fibers, protein fibers, etc.).

[0006]

[Object of the Invention] However, the fastness to light of conventional light resistance improving agents (such as sulfonated benzotriazole-type compounds, etc.) is still not sufficient. E.g., the fastness to light of the benzotriazole-type compounds with their hydroxyl group-containing phenyl group directly sulfonated that are described in Patent Disclosure No. Hei 1-[1989]-149,777 is low. This is probably attributable to the reduced ability to absorb ultraviolet light of the benzotriazole-type compounds due to the effects of the sulfonic acid group. Moreover, the fastness to light of the sulfonated benzophenone-type compounds is also low.

10 [0007] 2-(2'-Hydroxyphenyl)-2H-benzotriazole-type compounds having an aryl alkyl group sulfonated at p position at their 3' position or 5' position have been described in Patent Disclosure No. Hei 3-[1991]-118,373. These compounds, however, are difficult to synthesize and cannot be synthesized efficiently with a high yield. Furthermore, it is also difficult to synthesize sulfonated triazine-type compounds and they cannot be synthesized with a high yield.

[0008] Therefore, the objects of the present invention are to provide a light resistance promoting agent with excellent affinity for fibers and ability to impart the fastness to light to the fibers and to provide a method for its synthesis. The other objects of the present invention are to provide a light resistance promoting agent that has the

20 characteristics described above and that can be synthesized easily with a high yield and to provide a method of its synthesis. The additional object of the present invention is to provide a new benzotriazole compound.

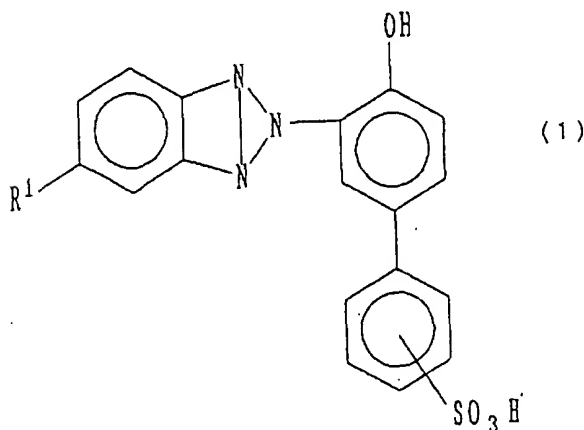
[0009]

[Means for Accomplishing the Objects] We carried out extensive studies and found that a benzotriazole-type compound with its phenyl group substituted at the 5' position sulfonated could be obtained with a high yield by the following procedures: among 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compounds, a 2-(2'-hydroxyphenyl)-2H-benzotriazole-type compound having a phenyl group at its 5' position as a starting compound was reacted with sulfuric acid and sulfonated. It was also found that this 2-(2'-hydroxyphenyl)-2H-benzotriazole type compound

30 having a sulfonated phenyl group at its 5' position showed excellent solubility for fibers and excellent fastness to light. These findings led us to develop the present invention. Namely, the present invention pertains to the sulfonated benzotriazole-type compounds that can be represented by formula (1) given below and their salts.

[0010]

[Chemical Formula 4]



(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

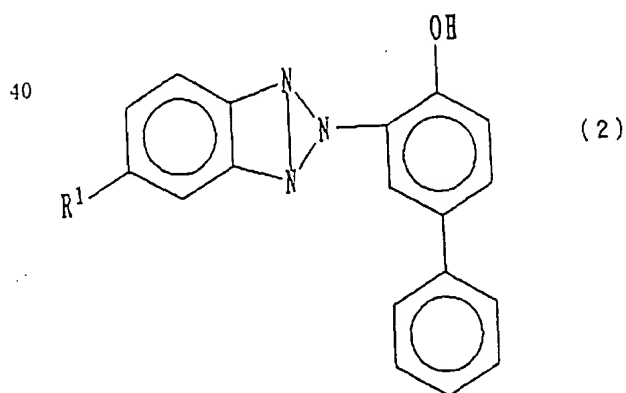
[0011] In the benzotriazole-type compounds of the present invention, as shown in formula (1) given above, a sulfonyl group is bonded to the phenyl group which is bonded to the phenyl group having a bonded hydroxyl group in a 2-(2'-hydroxyphenyl)-2H-benzotriazole type compound. Therefore, their effect as a light stabilizer (especially as an ultraviolet light absorbing agent) is high and their fastness to light is excellent. In addition, they are soluble in water and show excellent affinity for fibers (especially amide type fibers and protein fibers).

[0012] The benzotriazole-type compounds of the present invention are very suitable for use as a light resistance promoting agent for fibers and fiber products. The benzotriazole-type compounds show excellent affinity especially for polyamide type fibers and such protein fibers as wools and at the same time show excellent dyeing property and fastness to light.

[0013] The present invention also pertains to a method for the synthesis of a sulfonated benzotriazole-type compound that can be represented by formula (1) given below and its salts. In this method, the benzotriazole-type compound that can be represented by formula (2) given below is reacted with sulfuric acid and, if necessary, is converted to a salt form.

[0014]

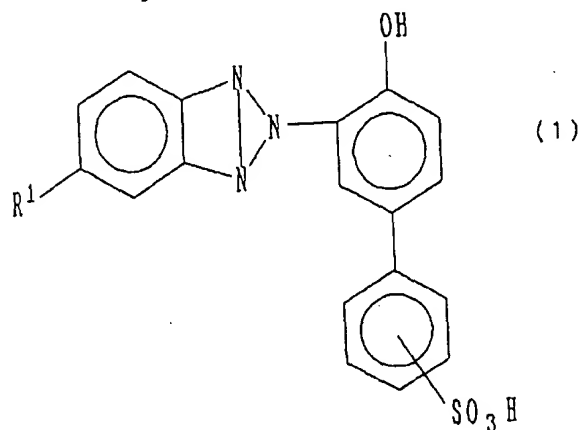
[Chemical Formula 5]



(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

[0015]

[Chemical Formula 6]



(in which R<sup>1</sup> denotes a hydrogen atom or a chlorine atom)

[0016] Using this method of synthesis, the benzotriazole-type compound of the present invention can be synthesized easily. Moreover, the benzotriazole-type compound of the present invention is a benzotriazole-type compound in which a sulfonated phenyl group is bonded to the phenyl group to which a hydroxyl group is bonded. In addition, a benzotriazole-type compound in which a phenyl group is bonded directly to the phenyl group to which a hydroxyl group is bonded is used as the raw material. This compound, therefore, is stable in an acidic state and little or no byproducts will form during the sulfonation reaction. Therefore, the benzotriazole compound of the present invention can be synthesized easily and effectively with a very high yield.

[0017] In contrast, in the synthesis of the benzotriazole-type compounds described in Patent Disclosure No. Hei 3-1991-118,373, namely, the benzotriazole-type compounds in which such an aryl alkyl group as a sulfonylated  $\alpha,\alpha$ -dimethylbenzyl group (cumyl group) is bonded to the phenyl group to which a hydroxyl group is bonded, a benzotriazole-type compound in which an aryl alkyl group is bonded to the phenyl group to which a hydroxyl group is bonded is used as the raw material. Therefore, byproducts are formed easily and the yield is low.

[0018]

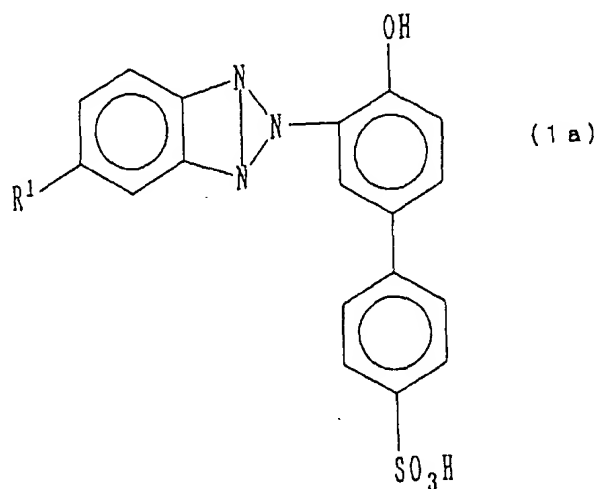
[Embodiment of Implementation of the Invention] In the sulfonated benzotriazole-type compound that can be represented by the said formula (1), there is no specific restriction as to the substituting position that can be sulfonated. In the phenyl group bonded to the 5' position of the phenyl group having a hydroxyl group, the sulfonation can be at any of the o positions (position 2 and position 6), the m positions (position 3 and position 5) or the p position (position 4) but preferably at the o positions or the p position or more preferably at the p position.

[0019] When the sulfonated benzotriazole-type compounds of the present invention are in a salt form, there is no specific restriction as to the kind of salts that can be used. E.g., they include alkali metal salts (such as sodium salts, potassium salts, etc.), ammonium salt, etc. Preferred salts are alkali metal salts (especially sodium salt and potassium salt). When the compounds are in the salt form, of course, the sulfonic acid group is in the salt form. E.g., it is in the form of such a sulfonate as an alkali metal salt of sulfonic acid.

[0020] Specifically, the sulfonated benzotriazole-type compounds of the present invention include, e.g., 2-[2'-hydroxy-5'-(p-sulphophenyl)phenyl]-2H-benzotriazole (also can be expressed as "3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid") that can be represented by formula (1a) given below or its salts (such as a sodium salt, a potassium salt, an ammonium salt, etc.).

[0021]

[Chemical Formula 7]



[0022] The sulfonated benzotriazole-type compounds of the present invention can be a mixture of the compounds with the position of sulfonation at the o position, the m position or the p position. Namely, the mixture may contain at least two of the compounds selected from the group consisting of the compounds with the position of sulfonation at the o position, the m position or the p position. However, it is preferable that the mixture is made of only the sulfonated benzotriazole-type compound having the sulfonic acid group only at the p position that can be represented by said formula (1a) or its salts.

[0023] Moreover, in the sulfonated benzotriazole-type compound of the present invention, the phenyl group having a hydroxyl group or the phenyl group having a sulfonic acid group may contain a substituting group (e.g., a chlorine atom, an alkyl group, an alkoxy group, etc.).

[0024] There is no specific restriction as to the method that can be used for the synthesis of the sulfonated benzotriazole-type compounds that can be represented by the said formula (1). The sulfonated benzotriazole-type compounds that can be represented by the said formula (1) can be obtained by reacting, e.g., the benzotriazole-type compounds that can be represented by the said formula (2) with sulfuric acid and, if necessary, the products thus obtained are converted to a salt form. In this method of synthesis, the benzotriazole-type compounds used as the raw material contain a hydroxyl group at the 2' position and at the same time contain a phenyl group at the 5' position. Therefore, during the sulfonation reaction, the phenyl group substituting at the 5' position is stable and this phenyl group at the 5' position is sulfonated. Especially, the p position of this phenyl group is attacked preferentially and sulfonated. In this method of synthesis, therefore, almost no side reaction will take place and the 2-[2'-hydroxy-5'-(sulfonated phenyl)phenyl]-2H-benzotriazole type compound that can be represented by the said formula (1) and their salts, especially the 2-[2'-hydroxy-5'-(p-sulfophenyl)phenyl]-2H-benzotriazole that can be represented by the said formula (1a) and its salt can be synthesized easily with a high yield.

[0025] As for the sulfuric acid used in this method of synthesis, concentrated sulfuric acid or fuming sulfuric acid may be properly used. In general, sulfuric acid is used in the form of an aqueous solution and there is no specific restriction as to its concentration. There is no specific restriction as to the amount of sulfuric acid used. However, it is desirable that more than 1 mole (e.g., 1-1,000 moles or preferably 10-500 moles or more preferably 50-300 moles) is used per 1 mole of the benzotriazole-type compound used as the raw material.

[0026] In the conversion of the product to a salt form, chlorides of alkali metals such as sodium chloride, potassium chloride, etc., hydroxides of alkali metals such as sodium hydroxide, etc., ammonia, etc., can be used properly. Of course, there is no specific restriction as to the amount of these compounds used as long as the amount used is sufficient for the conversion to a salt form. E.g., when the sulfonated benzotriazole-type compounds are to be converted entirely to a salt form, the amount used should be more than 1 mole for each mole of the sulfonated benzotriazole-type compound used.

[0027] There is no specific restriction as to the reaction temperature used during the sulfonation process. E.g., when concentrated sulfuric acid is used, the temperature can be 30-70°C or preferably 40-60°C.

[0028] The benzotriazole-type compound that can be represented by the said formula (2) [2-(2'-hydroxy-5'-phenyl phenyl)-2H-benzotriazole-type compound] can be obtained by reducing a nitroazo compound using a commonly used method. This nitroazo compound can be obtained by reacting o-nitrobenzene diazonium salt or its derivative with p-phenyl phenol (4-hydroxybisphenyl) (a coupling reaction). As mentioned above, the phenyl group introduced into the 5' position is stable even when heated at a high temperature under an acidic condition and thus almost no isomerization, cleavage or decomposition will occur. Therefore, the benzotriazole-type compounds that can be represented by the said formula (2) are compounds that are very suitable for synthesizing the target compounds.

[0029] The reaction of the said o-nitrobenzene diazonium salt or its derivative and p-phenyl phenol, namely, the reaction involved in the synthesis of the nitroazo compound, can be carried out using the procedure identical to that used for the reaction of o-nitrobenzene diazonium salt or its derivative and phenol. Moreover, as mentioned above, a commonly used reduction method may be used to reduce the nitroazo compound.

[0030] In addition, the sulfonated benzotriazole-type compound that can be represented by the said formula (1) can also be obtained by the procedure described below. First of all, p-phenyl phenol is sulfonated. The product thus obtained is allowed to react with o-nitrobenzene diazonium salt or its derivative and the product formed is reduced.



[0031] Specifically, p-phenyl phenol is reacted with sulfuric acid for sulfonation. The product is then converted to a salt form to obtain 4'-hydroxy-4-biphenyl sulfonate (e.g., a sodium salt of 4'-hydroxy-4-biphenyl sulfonic acid). This 4'-hydroxy-4-biphenyl sulfonate is reacted with o-nitrobenzene diazonium salt or its derivative to obtain a nitroazo compound (e.g., a sodium salt of 2-nitro-2'-hydroxy-5'-sulfophenyl azobenzene or its derivative). This nitroazo compound is then reduced to obtain a benzotriazole-N-oxide type compound. The product is further reduced and, if necessary, the sulfonate is converted to a sulfonic acid to obtain the benzotriazole-type compound of the present invention.

10 [0032] The reaction between 4'-hydroxy-4-biphenyl sulfonate and o-nitrobenzene diazonium salt or its derivative can be carried out with the use of the procedure identical to that used for the reaction between o-nitrobenzene diazonium salt or its derivative and phenol.

[0033] A commonly used method can be used to reduce the nitroazo compound or to reduce the benzotriazole-N-oxide type compound. E.g., the reduction can be carried out with the use of such a reducing agent as hydrazine, alcohol, etc., in the presence of a redox catalyst or an alkali. Moreover, in the case of reduction of the benzotriazole-N-oxide compounds, the reduction reaction can be carried out with the use of a method involving the use of zinc powder under an acidic condition.

20 [0034] An inert solvent may be used in the various reactions involved in the synthesis of the sulfonated benzotriazole-type compound (e.g., the reaction involving the synthesis of the nitroazo compound, the reduction reaction, etc.). Various solvents, e.g., such hydrophilic solvents as water, alcohol, etc., and such hydrophobic solvents as toluene, etc., may be used.

[0035] The reaction products can be separated or extracted from the reaction system with the use of a commonly used separation method or extraction method.

30 [0036] In the sulfonated benzotriazole-type compound, e.g., a 2-(2'-hydroxyphenyl)-2H-benzotriazole type compound, the sulfonic acid group is not directly bonded to the phenyl group having a hydroxyl group but the sulfonic group is bonded to the phenyl group which is bonded to the phenyl group having a hydroxyl group. Therefore, compared with the sulfonated benzotriazole-type compound described in Patent Disclosure No. Hei 1-[1989]-149,777 [2-(2'-hydroxyphenyl)-2H-benzotriazole type compounds with their sulfonic acid group directly bonded to the phenyl group having a hydroxyl group], the sulfonated benzotriazole-type compounds of the present invention are more effective and powerful light resistance promoting agents for fibers and fiber products and their fastness to light are excellent. This is because when the sulfonic acid group is directly bonded to the phenyl group having a hydroxyl group, the ultraviolet light absorbing capacity of benzotriazole can be reduced and blocked due to the effects of the minus ion on the sulfonic acid group. For this reason, 2-(2'-hydroxyphenyl)-2H-benzotriazole type compounds in which the sulfonic acid group is bonded through a cumyl group to the phenyl group having a hydroxyl group have been developed and described in Patent Disclosure No. Hei 3-[1991]-118,373. However, the yield of such compounds is very poor.

40 [0037] On the other hand, as mentioned above, the sulfonated benzotriazole-type compounds of the present invention are 2-(2'-hydroxyphenyl)-2H-benzotriazole type compounds in which the sulfonic acid group is bonded to the phenyl group to which the phenyl group having a hydroxyl group is bonded. Therefore, their synthesis is easy, little or no byproducts will form, and the yield is high.

[0038] Therefore, the sulfonated benzotriazole-type compounds of the present invention not only can be synthesized easily with a high yield but also show effective weather resistance and light resistance and excellent fastness to light.

50 [0039] Because the sulfonated benzotriazole-type compounds of the present invention contain a sulfonic acid group, their affinity for fibers (especially polyamide type fibers and such protein fibers as wools) is high. Therefore, the sulfonated benzotriazole-type compounds of the present invention are suitable for use as a light resistance promoting agent (especially as an ultraviolet light absorbing agent) for such polyamide fibers as polyamides and such protein fibers as wools. The sulfonated benzotriazole-type compounds of the present invention can be used individually or in combination of more than two types.

[0040] Moreover, when they are to be used for fibers or fiber products, they can be mixed directly with fibers or fiber products or they can be mixed with a dye first (namely, used with the dye in the same bath) and then mixed with fibers or fiber products.

[0041] Moreover, when the sulfonated benzotriazole-type compounds of the present invention are to be used as a light resistance promoting agent, they can be used in combination with other light stabilizers (e.g., other ultraviolet light absorbing agents, hindered amine type light stabilizers, etc.) or oxidation preventing agents (e.g., phenol type oxidation preventing agents, sulfur type oxidation preventing agents, phosphorus type oxidation preventing agents, etc.).

[0042] Furthermore, the sulfonated benzotriazole-type compounds of the present invention can be used concomitantly with a metal soap, a heavy metal inactivation agent, a nucleus forming agent, a plasticizer, etc.)

[0043]

[Actual Examples] The present invention will be explained in detail with the use of actual examples given below, but the present invention is not limited to these actual examples.

[0044] (Synthesis Example 1) Eighty g of o-nitroaniline, 122.4 g of 62.5% aqueous sulfuric acid solution and 600 mL of water were placed in a 1-L three-mouth flask. The mixture was cooled and kept at 0-5°C. To this mixture were added drop by drop 121.4 g of 34% aqueous sodium nitrite solution at a temperature in the range of 0-5°C over a period of 2 hours. The mixture was then stirred for 2 hours at the same temperature to obtain an o-nitrobenzene diazonium salt solution.

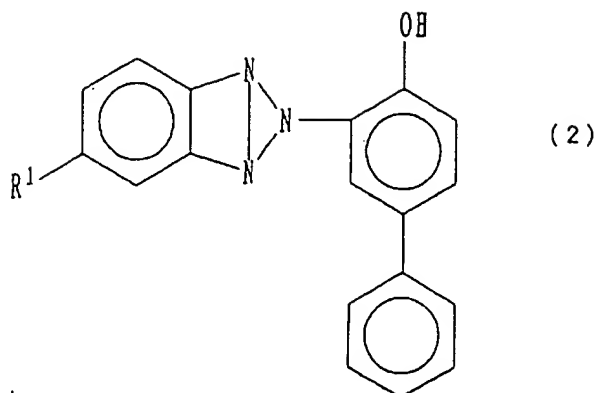
[0045] Separately, 101.6 g of p-phenyl phenol, 800 mL of methanol, 90 g of 48% aqueous sodium hydroxide solution and 400 mL of water were placed in a 3-L three-mouth flask and mixture was kept at 0-5°C. To this mixture was added the entire amount of the diazonium salt synthesized above at a temperature in the range of 5-10°C over a period of 2 hours while 50 g of sodium carbonate were added in 4 portions. The mixture was stirred for 2 hours. The crystals formed were separated by filtration, washed and dried to obtain 176 g of 2-nitro-2'-hydroxy-5'-phenyl azobenzene (purity: 99%, yield: 92.1%).

[0046] One hundred seventy-six g of 2-nitro-(2'-hydroxy-5'-phenyl) azobenzene thus obtained, 700 mL of water, 240 mL of toluene, 60.4 g of 48% aqueous sodium hydroxide solution and 0.8 g of hydroquinone were placed in a 2-L three-mouth flask and the mixture was heated to 50°C. To this mixture were added drop by drop 20 g of 80% hydrazine water at a temperature in the range of 50-75°C over a period of 1 hour and the mixture was stirred at 70-75°C for 2 hours. After the toluene layer was separated, the water layer was neutralized (pH 9) with the use of 33 g of 62.5% aqueous sulfuric acid solution. The crystals formed at 25°C were separated by filtration, washed and dried to obtain 147.5 g of 2-(2'-hydroxy-5'-phenyl phenyl)-2H-benzotriazole-N-oxide (purity: 98%, yield: 82.3%).

[0047] 121.4 g of the N-oxide compound thus obtained, 750 mL of toluene, 225 mL of water and 82.5 g of zinc powder were placed in a 2-L three-mouth flask and the mixture was heated to 55°C. To this mixture were added drop by drop 225 g of 62.5% aqueous sulfuric acid solution at a temperature in the range of 55-80°C over a period of 1 hour and the mixture was then stirred at 82-85°C for 2 hours. After the water layer was separated, 37.5 g of activated clay V<sub>1</sub> (a product of Mizusawa Kagaku Co.) were added and the mixture was stirred at a temperature above 110°C for 1 hour for decolorization. Thereafter, the mixture was subjected to a hot filtration process and 400 mL of toluene were recovered. One hundred mL of isopropyl alcohol were added and the crystals formed were separated by filtration, washed and dried to obtain 86.3 g of 2-(2'-hydroxy-5'-phenyl phenyl)-2H-benzotriazole (yield: 75%). This reaction product was analyzed by elementary analysis, etc. The results described below confirmed that the compound was 2-(2'-hydroxy-5'-phenyl phenyl)-2H-benzotriazole of the said formula (2).

[0048]

[Chemical Formula 8]



[0049] (Results of Analysis)

(Melting point)

Melting point: 158.1 °C

(Elementary analysis)

Calculated as  $C_{18}H_{13}N_3O$  (molecular weight 287)

C (carbon atom)      actually measured value: 75.31      (calculated value: 75.26)

H (hydrogen atom)      actually measured value: 4.42      (calculated value: 4.53)

N (nitrogen atom)      actually measured value: 14.70      (calculated value: 14.63)

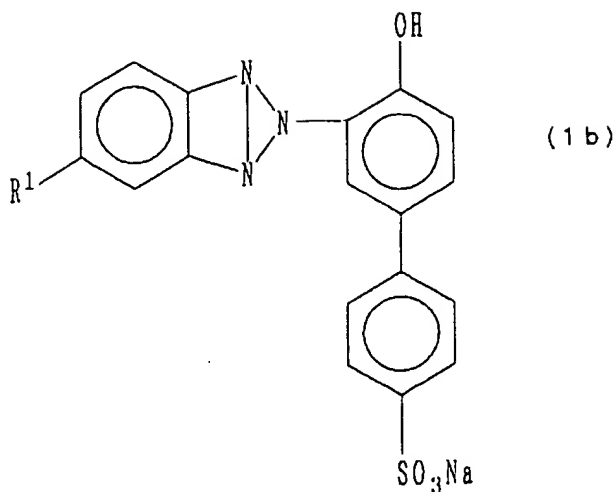
(Ultraviolet light absorption wavelength)

 $\delta 1$ : 348 nm $\delta 2$ : 301 nm

[0050] (Actual Example 1) Two hundred g of 98% concentrated aqueous sulfuric acid solution were placed in a 500-mL three-mouth flask and 50 g of 2-(2'-hydroxy-5-phenyl phenyl)-2H-benzotriazole were added at room temperature over a period of 30 minutes. The mixture was stirred at 50°C for 3 hours. To this mixture were added 25 g of sodium chloride over a period of 1.5 hours to obtain the product in a salt form. The solution was then diluted by adding it to a 2-L beaker containing 1,000 mL of water. The diluted solution was neutralized (pH 7) by adding 320 g of 48% aqueous sodium hydroxide solution. Twenty-five g of sodium chloride were then added to carry out a salting out process. After filtration, 67.5 g of light yellow crystals were obtained (yield: 99.6%). These light yellow crystals were recrystallized from hot water and the purified product was analyzed. The results given below confirmed that the product obtained was a sodium salt of 3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid.

[0051]

[Chemical Formula 9]



[0052] (Results of analyses)

(Elementary analysis)

Calculated as  $C_{18}H_{12}N_3O_4SNa$  (molecular weight 385)

C (carbon atom)	actually measured value: 56.1	(calculated value: 56.1)
H (hydrogen atom)	actually measured value: 2.1	(calculated value: 2.1)
N (nitrogen atom)	actually measured value: 10.1	(calculated value: 10.9)
S (sulfur atom)	actually measured value: 8.4	(calculated value: 8.3)

(Ultraviolet light absorption wavelength)

 $\delta 1$ : 341 nm $\delta 2$ : 276 nm

[0053] (Actual Example 2) Four hundred g of 98% concentrated aqueous sulfuric acid solution were placed in a 1-L three-mouth flask and 105.8 g of p-phenyl phenol were added at room temperature over a period of 30 minutes. To this mixture were added 52 g of sodium chloride over a period of 1.5 hours to obtain the product in a salt form. The solution was then diluted by adding it to a 3-L beaker containing 2,000 mL of water. The diluted solution was neutralized (pH 7) by adding 450 g of 48% aqueous sodium hydroxide solution. Fifty-two g of sodium chloride were then added to carry out a salting out process. After filtration, 162.5 g of yellowish white crystals were obtained (yield: 96%). These yellowish white crystals were found to be a sodium salt of 4'-hydroxy-4-biphenyl sulfonic acid.

[0054] Eighty g of o-nitroaniline and 122.4 g of 62.5% aqueous sulfuric acid solution and 600 mL of water were placed in a 1-L three-mouth flask. The mixture was cooled and kept at 0-5°C. To this mixture were added drop by drop 121.4 g of 34% aqueous sodium nitrite solution at 0-5°C over a period of 2 hours. Thereafter, the mixture was stirred at the same temperature for 2 hours to obtain an o-nitrobenzene diazonium salt solution.

[0055] 162.5 g of a sodium salt of 4'-hydroxy-4-biphenyl sulfonic acid obtained above, 90 g of 48% aqueous sodium hydroxide solution, 400 mL of water and 1,200 mL of methanol were placed in a 3-L three-mouth flask and the mixture was kept at 0-5°C. To this mixture were added drop by drop the entire amount of the diazonium salt solution obtained above at a temperature in the range of 5-10°C over a period of 2 hours while 50 g of sodium carbonate were added in 4 portions. The mixture was stirred for 2 hours. The crystals formed were separated by filtration, washed and dried to obtain 239 g (yield: 98%) of reddish brown crystals. The nitroazo compound thus obtained was found to be a sodium salt of 2-nitro-2'-hydroxy-5'-(p-sulfophenyl)phenyl azobenzene.

[0056] Two hundred thirty-nine g of nitroazo compound obtained previously, 800 mL of water, 300 mL of toluene, 75 g of 48 % aqueous sodium hydroxide solution and 1.0 g of hydroquinone were placed in a 2-L three-mouth flask and the mixture was heated to 50°C. To this mixture were added drop by drop 25 g of 80 % hydrazine water at a temperature in the range of 55-80°C over a period of 1 hour and the mixture was stirred at 75-80°C for 2 hours. After the toluene layer was separated, the water layer was neutralized (pH 8) with the use of 41 g of 62.5 % aqueous sulfuric acid solution. The crystals formed were separated by filtration, washed and dried to obtain 192.5 g (yield: 82 %) of a triazole-*N*-oxide compound in the form of yellow crystals corresponding to the targeted material [sodium salt of 3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid].

10 [0057] 192.5 g of the triazole-*N*-oxide compound obtained previously, 1,000 mL of water and 85 g of zinc powder were placed in a 2-L three-mouth flask and the mixture was heated to 55°C. To this mixture were added drop by drop 250 g of 62.5 % aqueous sulfuric acid solution at a temperature in the range of 55-80°C over a period of 1 hour and the mixture was then stirred at a temperature in the range of 82-85°C for 2 hours. The mixture was then subjected to a hot filtration process and cooled. The solution was neutralized (pH 7) with the use of 50 g of 48 % aqueous sodium hydroxide solution. The crystals formed were separated by filtration, washed with water and dried to obtain 63.1 g (yield: 34 %) of a sodium salt of 3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid that can be represented by the said formula (1b) in the form of light yellow crystals.

20 [0058] The target product obtained from Actual Example 2 [sodium salt of 3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid] and the target product obtained from Actual Example 1 [sodium salt of 3'-(2H-benzotriazole-2-yl)-4'-hydroxy-4-biphenyl sulfonic acid] were analyzed by TLC (thin layer chromatography). They gave spots on the same location on TLC, confirming that these two products were identical.

[0059] (Evaluation)

30 (Test for Fastness to Light) The benzotriazole-type compounds obtained from Actual Examples 1 and 2 were used as a light resistance promoting agent and the fastness to light of fibers was evaluated according to the procedure described below. In Comparison Example 1, the same test for the fastness to light was also carried out except that the light resistance promoting agent was not used (test for the fastness of light of dye) to evaluate the fastness to light.

40 [0060] (For Polyamide Fibers) Ten g of Nylon (6-6) taffeta were dyed by boiling for 40 minutes in the same bath containing 0.2 % (owf: on the weight of fiber) of "Lanasyn Bordeaux BL 200 %" (brand name, manufactured by Sando Co.), 3 % (owf) of ammonium sulfate, 1 % (owf) of "Lyogen UL liq" (brand name, manufactured by Sando Co.) and 1 % (owf) of a light resistance promoting agent with a bath ratio of 1:30. For the post-treatment, the fabric was boiled for 30 minutes in 1 % (owf) of "Lyogen NN liq" (brand name, manufactured by Sando Co.) with a bath ratio of 1:20 and dried to obtain a polyamide dyed fabric. A fastness to light test was carried out according JIS 0841 (1974) to evaluate the fastness to light of the fabric. The fastness of the fabric dyed with the benzotriazole-type compound obtained from Actual Examples 1 and 2 was of grade 7-8 whereas that of the fabric from Comparison Example 1 (dyed fabric without the light resistance promoting agent) was of grade 7.

50 [0061] (For Wool Serge) Ten g of wool serge fabric were dyed by boiling for 40 minutes in the same bath containing 0.11 % (owf) "Lanasyn yellow 2RL 180 %" (brand name, manufactured by Sando Co.), 3 % (owf) of ammonium sulfate, 1 % (owf) of "Lyogen UL liq" (brand name, manufactured by Sando Co.) (C. I. Acid Orange 80), 0.10 % (owf) of "Lanasyn Bordeaux BL 200 %" (brand name, manufactured by Sando Co.) (C. I. Acid Red 217), 0.16 % (owf) of "Lanasyn Black BRL 200 %" (brand name, manufactured by Sando Co.) (C. I. A Acid Black 132), 10 % (owf) of anhydrous Glauber's salt, 4 % (owf) of ammonium sulfate, 1 % (owf) of "Lyogen UL liq" (brand name, manufactured by Sando Co.) as an aid and 1 % (owf) of a light resistance promoting agent with a bath ratio of 1:30. For the post-treatment, the fabric was boiled for 30 minutes in 1 % (owf) of "Lyogen NN liq" (brand name, manufactured by Sando Co.) with a bath ratio of 1:20 and dried to obtain a dyed wool fabric. A fastness to light test was carried out according JIS 0841 (1974) to evaluate the fastness to light of the fabric. The fastness to light of the fabric dyed with the benzotriazole-type compound obtained from Actual Examples 1 and 2 was of grade 7 whereas that of the fabric from Comparison Example 1 (dyed fabric without the light resistance promoting agent) was of grade 6.

[0062] Therefore, when the benzotriazole-type compound of the present invention is used in polyamide fibers or wools, excellent fastness to light can be obtained and discoloration of fibers can be prevented for a long period of time.

[0063]

[Effect of the Invention] Therefore, the fastness to light of the compounds associated with the present invention is excellent. The method of their synthesis is easy and they can be synthesized with a high yield. For these reasons, when the sulfonated benzotriazole-type compounds of the present invention are used in fibers or fiber products, discoloration or color change of fibers can be prevented for a long period of time.

10